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CORRELATING EXPERIMENTAL RESULT WITH THEORETICAL CALCULATIONS ON: EFFECTS OF SUBSTITUENTS ON EXTRACTION EFFICIENCY OF NAPHTHALENE BASED CHELATES (MONO- AND DI-SUBSTITUTED) FOR Hg(II), Cd(II), AND Pb(II) DIVALENT IONS

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Abstract

Three of the most dangerous and toxic metal ions—Hg(II), Cd(II), and Pb—were chelated using the naphthalene derivatives (NPC, NPM, NPS, DNP, DMS, and NPH) in this study (II). By calculating the percent extraction for each individual interaction between the provided chelates and each of the stated ions, the effectiveness in capturing (extracting) for the three metal ions was assessed. DNP has an excellent extractor for the three metal ions (77. 2, 31.58, 42.0% percent extraction for Hg, Cd, and Pb, respectively); NPM has a good extractor for Hg ions in particular; however, NPS has a poor extractor for all three ions (23.634.6% 11.706% 1 6.204.5% for Hg, Cd, and Pb, respectively. The structure of the chelate, the structure of the compound formed, the type and number of substituents present on the chelator, which are important in determining stability, the type and number of donor atoms within the chelate were found as parameters by which the extraction efficiency was found to be dependent (oxygen is better as a donor atom than nitrogen) and This affects the charge density distribution on the surface of the chelate on how well it binds to metal ions as well as other chelating properties, such as chelate shape, linearity, and stability.This conclusion was reached following the execution of theoretical computations. APT-Charge density on donor atoms suggests that increasing the charge density on the donor atom is crucial for improving the efficiency of the extraction. DNP chelate is one example which shows good extraction efficiency for all of the three ions.

Keywords: Naphthalene, Extraction Capacity, Mercury, Cadmium, Lead.

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Introduction

Environmentalists in general and chemists in particular are well aware of heavy metal pollution and the detrimental impact it has on living things(Ayansina Segun Ayangbero & Olubukola Oluranti Babalola,2017). These elements' accumulative concentrations, which tend to rise in the environment with the expansion of industrial activity, are a key factor in determining how dangerous they are(Al-Blawi etal.,2018). For instance, the nuclear(Akpor et al.,2014), metallurgical(Barakat, 2011), tannery(Islam et al.,2013), mining(Gaikwad et al.,2018), cosmetics(Sani et al.,2016), insecticides(Dafaelsee et al2007), photography(Gautam et al.,2014), textile[Buthelezi et al.,2012], paint(Malakootian et al.,2009), dye(enkatsham et al. 2018), and battery industries(Hegazi,2013) often discharge heavy metal ions.

According to the findings and because of their impacts on humans specifically(Agrawal,2012), and other living things generally(Gupta2016), removing them from polluted media has been a major concern for many interested researchers. Divalent ions of lead (Pb), cadmium (Cd), and mercury (Hg) are among the most dangerous heavy metals, particularly for water resources(Karri,2016). This is due to their high toxicity, lack of biodegradability, and buildup in living systems(Taghipour et al.,2016), which ultimately result in catastrophic illnesses and abnormal organ function(Jan et al.,2016). As a result, one of the most significant and difficult problems in the field of water pre-treatments is the detection and extraction of the aforementioned metal ions from the affected areas(Soriano-Disla et al.,2010).

It is well known that cyclic compounds of fused aromatic rings with nitrogen and oxygen donor atoms have greater electron density levels than their carbocyclic counterparts. These compounds can thus discharge additional delocalized electrons into the system to which they belong. They have so attracted increasing interest in recent years(Al Abdel Hamid et al,2015) as possible and necessary options for stabilizing metal ions in coordination chemistry. The group of naphthalene substituted derivatives, which includes donor atoms like nitrogen and oxygen atoms with free electrons in their valence shells, is one of these molecules. It is believed that adding N and O atoms to these molecules will increase their electron density and consequently, contributes more to the overall electron-donating activity of the ligand. As a result, substituted derivatives of naphthalene are frequently used as chelates in coordination complexes and have long been regarded as a benchmark for understanding the binding behavior of transition metal ions in particular (Al Abdel Hamid et al,2015).

In earlier research of a similar nature (Al Abdel Hamid (2010); Al Abdel Hamid, (2018), Al Abdel Hamid et al.,(2016)), we found that theoretical calculations were highly useful in understanding how different parameters interact to alter the kinetics of electronic delocalization over the chelate structure. In this study, we seek to explore (and hence advance our understanding of) the binding efficiency of the aforementioned simple naphthalenes comprising nitrogen and oxygen donors as chelators (extractors) toward the environmentally significant divalent heavy metal ions, Hg(II), Cd(II), and Pb (II). This systematic investigation into the complexation of the advanced cations with mono- and di-substituted naphthalene derivatives is actually carried out.

The purpose of this investigation is to determine whether the substituent change has an impact on the proposed naphthalene derivatives' ability to bind and to extract. This occurs when the targeted metal ions Hg(II), Cd(II), and Pb(II) interact in an aqueous solution.

Problem statements

Lead, cadmium, and mercury are still removed from contaminated media with the utmost care because they are considered to be very harmful to living things and the environment as a whole(Campbell et al.,1998). Chelation is frequently used to remove them from the afflicted areas efficiently and quantitatively. A chelate (or chelator) is a substance that binds a metal ion to two or more donor sites in coordination chemistry to create a stable ring complex. The term "chelation therapy" refers to the application of chelate chemistry in medicine to the simple process of removing heavy metals from the body by binding to a therapeutic chelation agent. Chelation agents' affinity for the desired metal, also referred to as the "Bchelate effect" in inorganic chemistry, is its key feature. naphthalene based chelators are a good example(Al Abdel Hamid,2019)

In the report recently published by the doctor (**Amer Jafer Al Abdel Hamid)** who supervised my thesis Amer, hamid (2018).The effectiveness of extracting toxicants Divalent metal ions Hg(II), Cd(II), and pb(II) from four diacid chelates namely(malonic (MAL) and succinic (SUC), adipic (ADP), and superic acids (SUP)) has been experimentally evaluated as a function of the -CH2 units that bind between two carboxyl groups are attached to the tails of the forming chain. The report mentioned came to the conclusion that the extraction. The quantity of -CH2 units connecting the two COO groups affects how effective the four chelators are accurately, It was discovered that the V Order, MAL (from one -CH2 unit), SUC (from two -CH2 units), ADP (from four —CH2 units), and SUP (from six - CH2 units) were all improved by the elimination of the three metal ions using the of metalchelating method (quantitative extraction). The efficiency of extraction is paralleled by this arrangement. All interactions between MAL, SUC, ADP, and SUP with the metal ions Hg (II), Cd (II), and Pb (II), where each metal is dioecious chelate interacted independently, resulted in a chelate and a number of -CH2 units. This finding was interesting and believed to deserve further investigation.

Methodology

2.1.general

The following procedures and methodologies were used in this research study to first gather the data and then analyze it. They are as follows: Gravimetric analysis, IR spectroscopy, atomic analysis, using Guassian 09 for theoretical calculation, establishing a connection between experimental and theoretical outcomes. In order to (a) assess the accumulation of electron density on the donor atoms within the chelate, (b) draw the distribution surfaces of the charge density on the chelate as a whole, (c) gauge the chelate's stability, and (d) ascertain the vibrational frequencies of the significant functional groups contained in the chelate, theoretical calculations were carried out.

The following substances were bought from Aldrich: 1-naphthoic acid (NPC), 1-naphthylamine (NPM), 1-naphthylisocynate (NPS), 1,8-diamino naphthalene (DNP), 1-nitroso-2-naphthol (DMS), and 2-nitroso-1-naphthol (NPH). The metal chlorides of Hg(II), Cd(II), and Pb(II) (99%), as well as Na2S (anhydrous), were likewise acquired from Aldrich and used exactly as received. The metal chlorides were desiccated before use, while the ligands NPC, NPM, NPS, DNP, DMS, and NPH were kept in the refrigerator. Every ingredient was applied exactly as it had been

2.2. Preparation of (1-Naphthoic acid) metal complexes with Hg(II), Cd(II) and Pb(II)

NPC (0.8700 g, 5.05 mmol) was dissolved in (80 mL of 0.1 M; 8.00 mmol) NaOH to obtain the disodium salt of the ligand; Na_2NPC. An aqueous solution of mercury chloride, lead and cadmium ion dissolved in 50 ml HO was added to the basic solution of NPC in NaOH. The formed product was isolated by vacuum filtration, and washed thoroughly with 3

parts (20 mL) distilled water, followed by washing with similar parts ethanol. Finally, the collected sediment was dried in an oven at 110 °C overnight.

Calculating the actual return on the output.

The amount (in mmoles) of unreacted metal ion was determined gravimetrically by addition of excess amount of anhydrous sodium sulfide (dissolved in minimum H2O) to the combined filtrate and washings collected during the separation process. Mercury, Cadmium and Lead divalent ions are known to react(Al Abdel Hamid et al.,2010)

quantitatively to form metal sulfide. The formed metal sulfide (mercuric sulfide; HgS in case of mercury interaction), was then isolated by vacuum filtration, washed and dried to complete dryness (until reaching constant weight) at 120C°. Then the melting point of all complexes was calculated.

Aqueous solution of NaOH (0.1M) was prepared and standardized with potassium hydrogen phthalate (KHP) utilizing the well-known standard procedures(Gary D. Christian,1994). In addition, solution of the Na_2NPC salt was prepared by adding 1.5 equivalents of NaOH to the NPC aqueous solution.

2.3. Method of extraction

Excess anhydrous Na2S was used to treat the liquid phase after it had been separated from the solid material and the interaction between the metal salt and the chelate solution was complete. The solid metal sulfide that had precipitated was then separated, cleaned, and dried at 1200°C to a consistent weight (complete dryness). By calculating the difference between the initial mmoles of the free metal ion in the liquid phase and the mmoles of the metal precipitated in the form of metal sulfide, the extent of complexation of the metal ion by each of the included chelates was determined gravimetrically.

2.4.Control experiment

Control tests were carried out in earlier research to assess the quantitative recovery of unchelated Hg(II), Cd(II), and Pb(II) ions in aqueous solution(Gary D. Christian,1994). Their aqueous solutions underwent treatment with extra anhydrous Na2S, and the percentage recovery of the metal ions in the form of metal sulfides was 99.1% 0.5%.

2.5. Ab initio calculations

Using the Gaussian 09 program, ab initio calculations of the model structures of the used chelates NPC, NPM, NPS, DNP, DMS, and NPH were carried out (Gary D. Christian(1994); Frisch et al.,2003). Utilizing the DFT (Gu et al.,(2010); Parajuli.(2012)) approach and the B3LYP (Fattahi, & Shakorian Fard Jahromi ,2009) functional, structural optimization was achieved. The necessary calculations have been carried out using the density functional theory (DFT) and time dependent density functional theory (TD-DFT). In the vacuum, basis sets for the B3LYP technique with LANL2DZ were also used (Fattahi, & Shakorian Fard Jahromi ,2009). Vibrational frequency calculations came after the optimization of the geometry (Senevirathne et al.,2011); Al Abdel Hamid, (2013)). The charge distribution on the atoms of the examined chelates was calculated using the APT (Atomic partial tensor) model [De Angelis et al.,(2013); Nazeeruddin et al.,(2005)). The Gaussian 09 application [Ghosh et al.(,2006); Al Abdel Hamid et al.,(2014)) was used to perform all calculations on a Toshiba-Satellite i5 Dual Core running Windows 7. In theoretical computations of TD-DFT and vibrational spectra, geometry optimization is regarded as the key stage. When vibrational frequencies and intensities were calculated over all geometries at the same theoretical levels as those employed for geometry optimization, they all converged precisely.

3. Results and Discussion

3.1 IR-spectroscopy is utilized to help monitoring the style of coordination and point of attachment between the coordinated metal ion and the involved chelate

3.1.11 IR-spectroscopy for Naphthoic acid (NPC) complexes

The NPC chelate has the -COOH group as the basic functional group eligible for binding with the positive metal centers. Therefore, our focus will be paid for the spectral changes taking place in the frequency range of are characterizing this 1 -this group. The two bands at 1670 and 1300 cmcarboxylate group, Figure 1(Red). After interaction with the metal ions, the Blue almost disappeared band is greatly reduced (1 -1670 cmGreen, Violet), indicating the occurrence of coordination between the two oxygens of the carboxylate group and each of the mentioned ions

Comparing the IR-spectrum of the free NPC, Figure 1(Red) with the spectra of the three complexes, Figure 1(Blue, Green, Violet), indicates that, attachment of the NPC chelate with the three ions, is further evidenced the free chelate. This band of1 -1300 cmby the blue shift observed in the 1 -cm17 14-band has blue shifted to appear within the frequency range 1347spectra 4(Blue, Green, Violet) upon complexation. Based on the calculated APT-partial electron density and shown in Figure 11) the two carboxylate oxygens become equivalent when the -COOH acid group is deprotonated. With respect to the extraction efficiency of the NPC chelate toward the three ions, the values of percent extraction reveals that NPC was better removal for Pb ions compared to Hg or Cd ions. This can be understood in terms of the hardness close matching between the carboxylate oxygens from one side and Pb ion relative to Hg and Cd ions, from the other side.

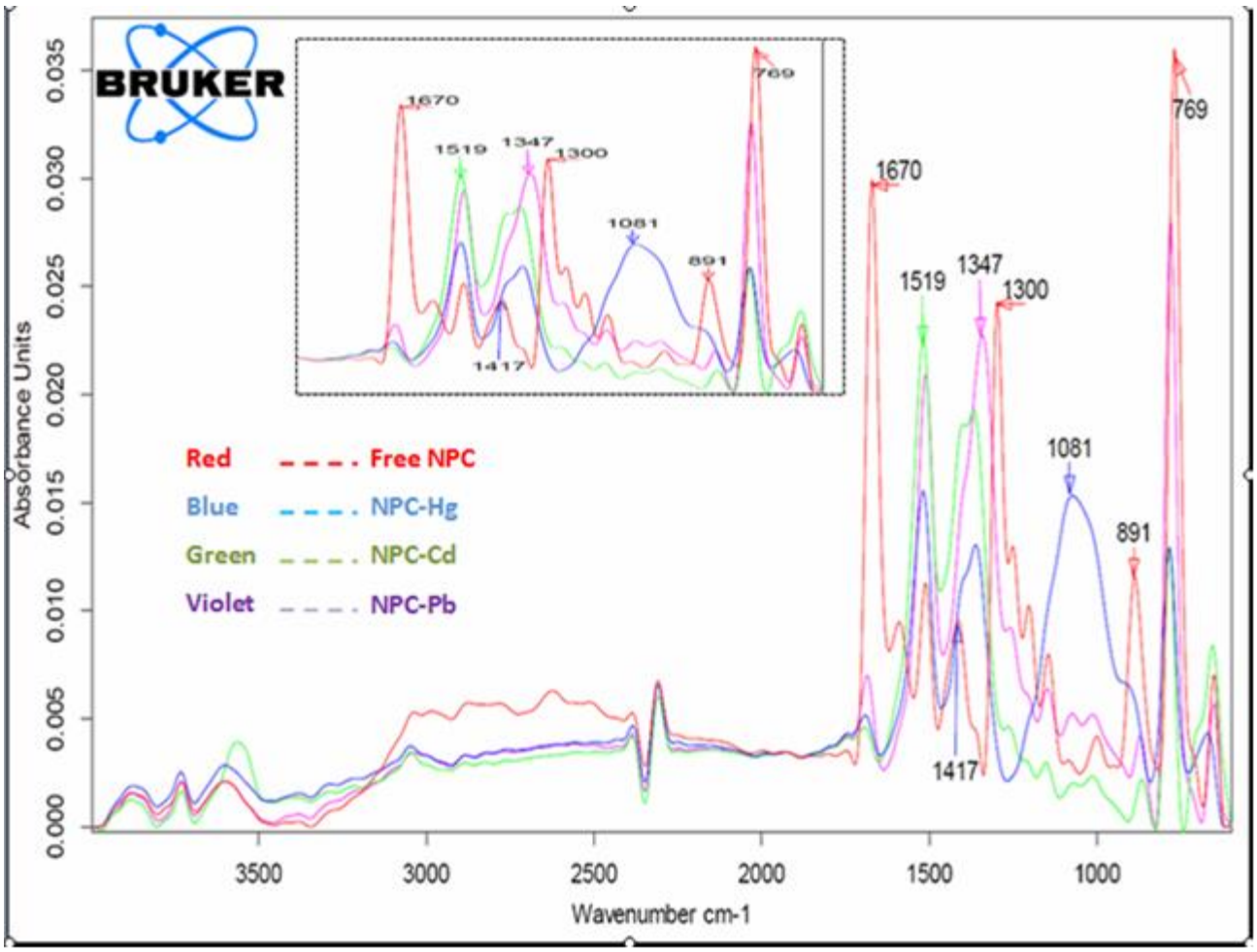


Figure 1. IR-spectra of: (Red) free NPC chelate, (Blue) NPC-Hg(II)(Green)NPC-Cd(II) and (violet) NPC-Pb(II) complexes

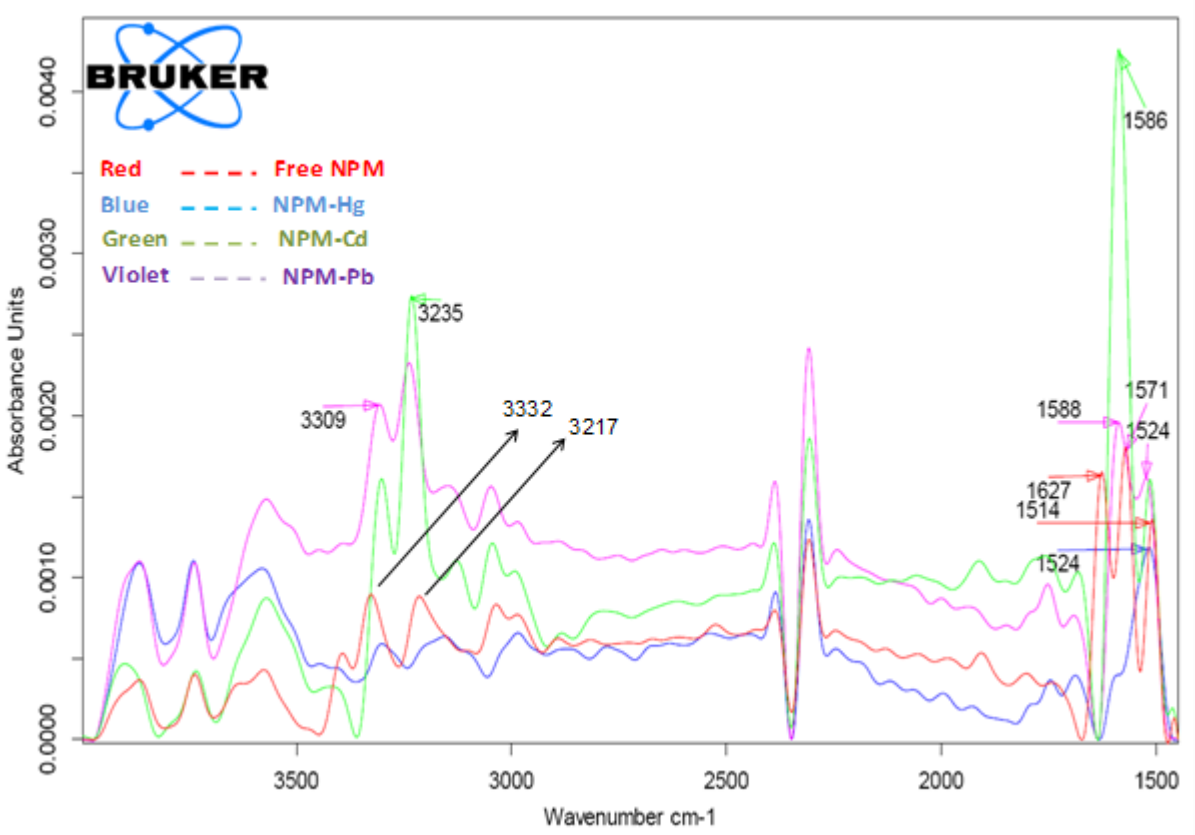


Figure 2. IR-spectra of: (Red) free NPM chelate, (Blue) NPM-Hg(II)(Green)NPM-Cd(II) and (violet) NPM-Pb(II) complexes

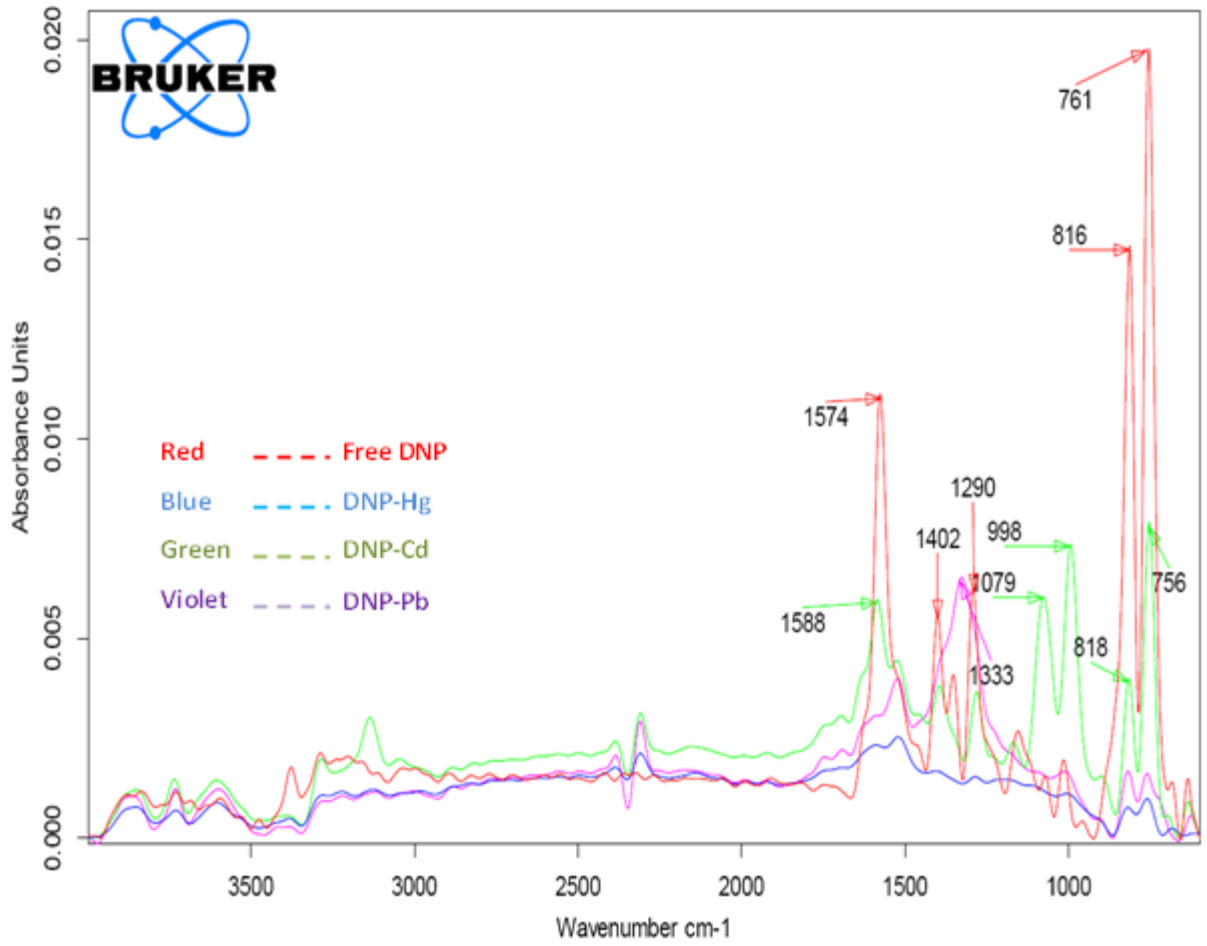


Figure 3. IR-spectra of: (Red) free DNP chelate, (Blue) DNP-Hg(II)(Green)DNP-Cd(II) and (violet) DNP-Pb(II) complexes

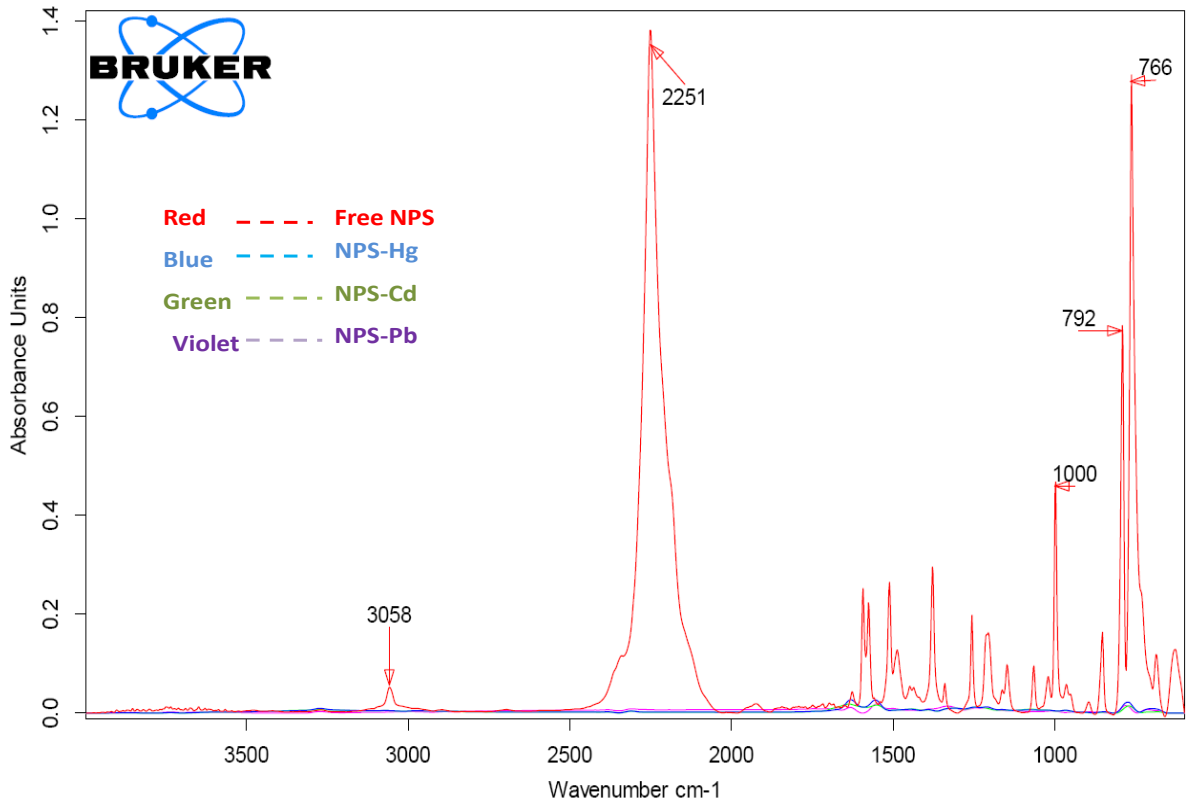


Figure 4. IR-spectra of (a) (Red) free NPS chelate (b) (Blue) NPS-Hg(II) (c) (Green) NPS-Cd(II) and (Violet) (d) NPS-Pb(II) complexes

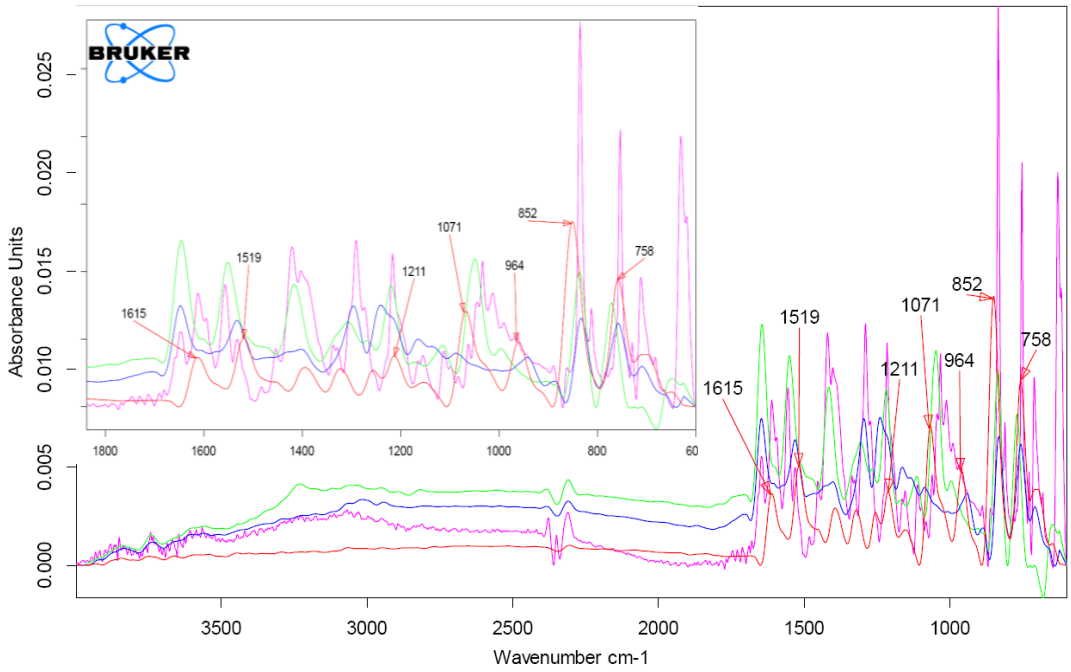


Figure 5. IR-spectra of (a) free DMS chelate (b) DMS-Hg(II) (c) DMS-Cd(II) and (d) DMS-Pb(II) complexes

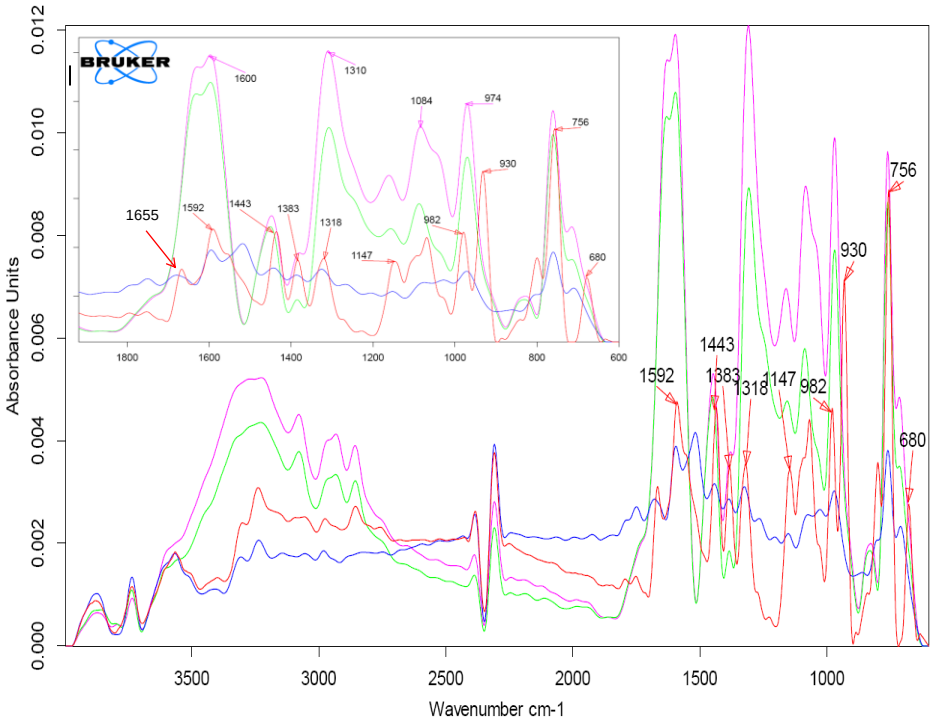


Figure 6 IR-spectra of (a) free NPH chelate (b) NPH-Hg(II) (c) NPH-Cd(II) and (d) NPH-Pb(II) complexes

3.2. Results of Theoretical Calculations

Theoretical calculations, such as mapping the electron density over the chelate structure and other factors, will be done in addition to the study's experimental component. To accomplish a number of goals, including: (1) improving understanding of the binding effectiveness of the listed chelates; (2) learning the effects of the tethered substituents (in terms of substituent position, type, and number); and (3) assessing the chelate's capacity as an extractor for the specified metal ions by calculating the percent e, the gathered theoretical results will be toned and correlated with the experimental findings.

3.2.1Analyses of optimized geometry parameter

The fully optimized geometries of the studied chelates are shown in Figure7, whereas the values of the optimum energies are included in Table 1. Energy minimum structures resulted from all calculations of the six naphthalene derivatives are true as deduced by the absence of the imaginary vibrations in output files of the frequency calculations. Furthermore, the surfaces of the APT-partial charge density distribution over donor atoms of the included chelates are shown in Figure 7

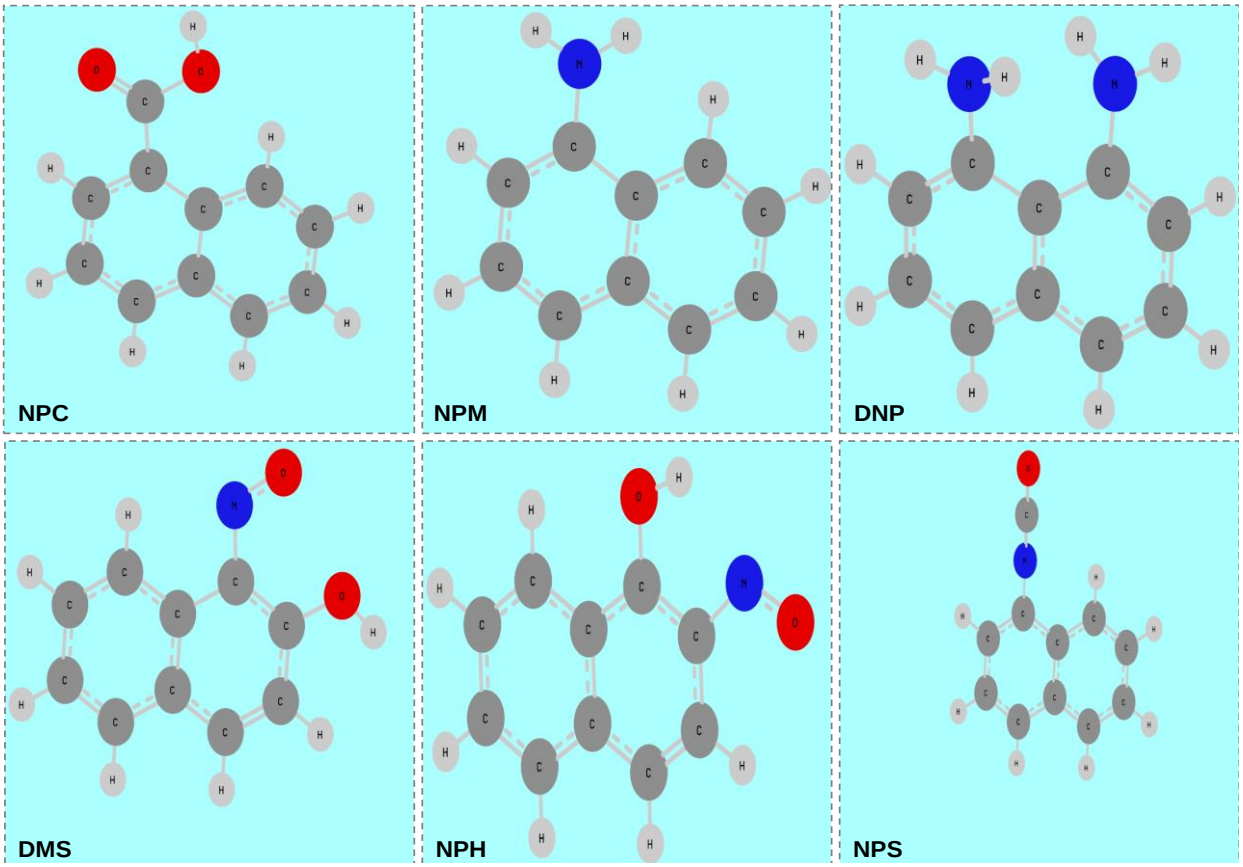


Figure 7. Optimized geometric structures of the studied chelates: (NPC), (NPM), (DNP), (DMS), (NPH) and (NPS) using DFT method

3.2.APT-Charge density:

Correlating the values of percent extraction with the APT-Charge density on donor atoms, indicate that charge density accumulated on the donor atom is essential in enhancing the extraction effectiveness. For example DNP chelate (which shows good extraction efficiency for all of the three ions) has donor atoms which are more electron rich than NPS chelate. In comparison, NPS was not effective enough toward extracting the same ions, Tables 3 and 4. Another worthing comparison is between DMS and NPH. In NPH the two oxygens are more electron dense than the two in DMS, and in consequence NPH has shown better extraction efficiency than DMS, see Tables 1

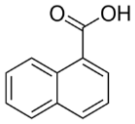
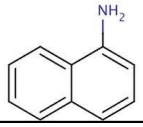
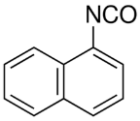
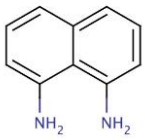
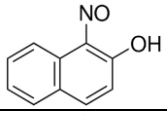
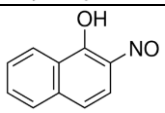
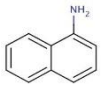
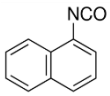
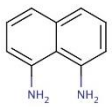
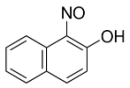
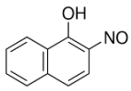
No.	Ligand	Structure	Optimum Energy (a.u)	APT-partial charge on donor atoms (a..u)
1	1-naphthoic acid (NPC)		-574.37627350	- 0.710 (O of O-H)
2	1-naphthylamine (NPM)		-441.18300027	- 0.827 (N of NH_2)
3	1-naphthylisocynate (NPS)		-553.28189497	- 0.526 (N of N=C) - 0.560 (O of C=O) + 0.861 (C of C=O)
4	1,8-diamino naphthalene (DNP)		-496.52982785	- 0.760 (N of $NH_{2\ (1)}$) - 0.760 (N of $NH_{2\ (2)}$)
5	1-nitroso-2-naphthol (DMS)		-590.30595413	+ 0.521 (N of N=O) - 0.504 (O of N=O) - 0.650 (O of O-H)
6	2-nitroso-1-naphthol (NPH)		-590.32791718	+ 0.669 (N of N=O) - 0.648 (O of N=O) - 0.671 (O of O-H)

Table 1. Calculated optimum energy and atomic-polar-tensor (APT) partial charge of donor atoms

3.3.Chelate Stability: As can be clearly seen in Table 2, chelate optimization energy is related to hardness of the chelate, where both factors go in parallel to each other. All hard chelates (NPC, NPS, DMS and NPH) possess higher optimization energy compared to the soft NPM and DNP chelates. If we correlated the chelate stability (measured in terms of the calculated optimization energy) with the extraction effectiveness of the chelate, we can say that chelate effectiveness as extractor becomes less as stability goes up. For example, and as in Table 5, when we compare DNP with NPC, we find that DNP has less optimization energy than NPC, however, DNP was more motivated toward binding and thus was better extractor than NPC

Table 2. Various parameters that are assumed to affect extractability

L	Structure	Cplx(% Ex)	Stab (E_{stab})	Sbt	Donor atom	Hrd	M: L Ratio
NPC		NPC-Hg(24.56%) NPC-Cd(35.14%) NPC-Pb(60.90%)	High (-574)	Mono	O, O	Hard	1:1 1:1 1:2
NPM		NPM-Hg(83.8%) NPM-Cd(10.30%) NPM-Pb(15.60%)	High (-441)	Mono	N	Soft	1:2 1:2 1:2
NPS		NPS-Hg(23.6%) NPS-Cd(11.70%) NPS-Pb(16.20%	High (-553)	Mono	O	Hard	1:2 1:2 1:2
DNP		DNP-Hg(77.2%) DNP-Cd(60.37%) DNP-Pb(58.89%)	High (-496)	Di	N, N	Soft	1:1 1:1 1:1
DMS		DMS-Hg(31.8%) DMS-Cd(74.86%) DMS-Pb(42.01%)	High (-590)	Di	O, O	Hard	1:1 1:1 1:1
NPH		NPH-Hg(30.73%) NPH-Cd(82.75%) NPH-Pb(20.45%)	High (-590)	Di	O, O	Hard	1:1 1:2 1:2

L = ligand, Cplx(% Ex) = complex (percent extraction), Stab (E_{stab}) = stability (energy), Sbt = substituent, Hrd = hardness,

3.4.Analyses of the APT-charge distribution

Figure8, shows the plot of APT-charges and images of charge-density distributions of the six chelates. Images in the Figure indicate that: In all chelates, the charge density is predominantly localized on donor atoms within the chelate. These are, oxygens in NPC, DMS, NPS and NPH chelates and nitrogens in NPM and DNP chelates . In general, the amount of charge density localized in the vicinity of oxygen-donor atoms is more than that localized on nitrogen-donor atoms. This is clearly seen by comparing the intensity and size of the red spot around oxygen relative to that around nitrogen as shown by the images of the APT-charge density surfaces in Figure 8. , the amount of charge density withdrawn from the naphthalene substrate is more when oxygen is the donor than when nitrogen was the donor. This can be observed from the intensity of the yellowish-green color region appearing specifically in images of NPC compared to NPM. In charge density surfaces of the NPM, the intensity of the yellowish-green color region is more intense compared to that in NPC, indicating that, the amount of charge density withdrawn from the naphthalene substrate toward nitrogen donor atom is much less compared to that heading toward oxygen donor atom in NPC. In part, this might be attributed to the greater electronegativity of oxygen atom compared to nitrogen atom we expect oxygen atom to be more effective toward binding the incoming metal ions (especially the hard ones) than nitrogen. Where, owing to the greater enrichment with the electron density, oxygen atoms rather become harder compared to nitrogen atom of less delocalized electron density

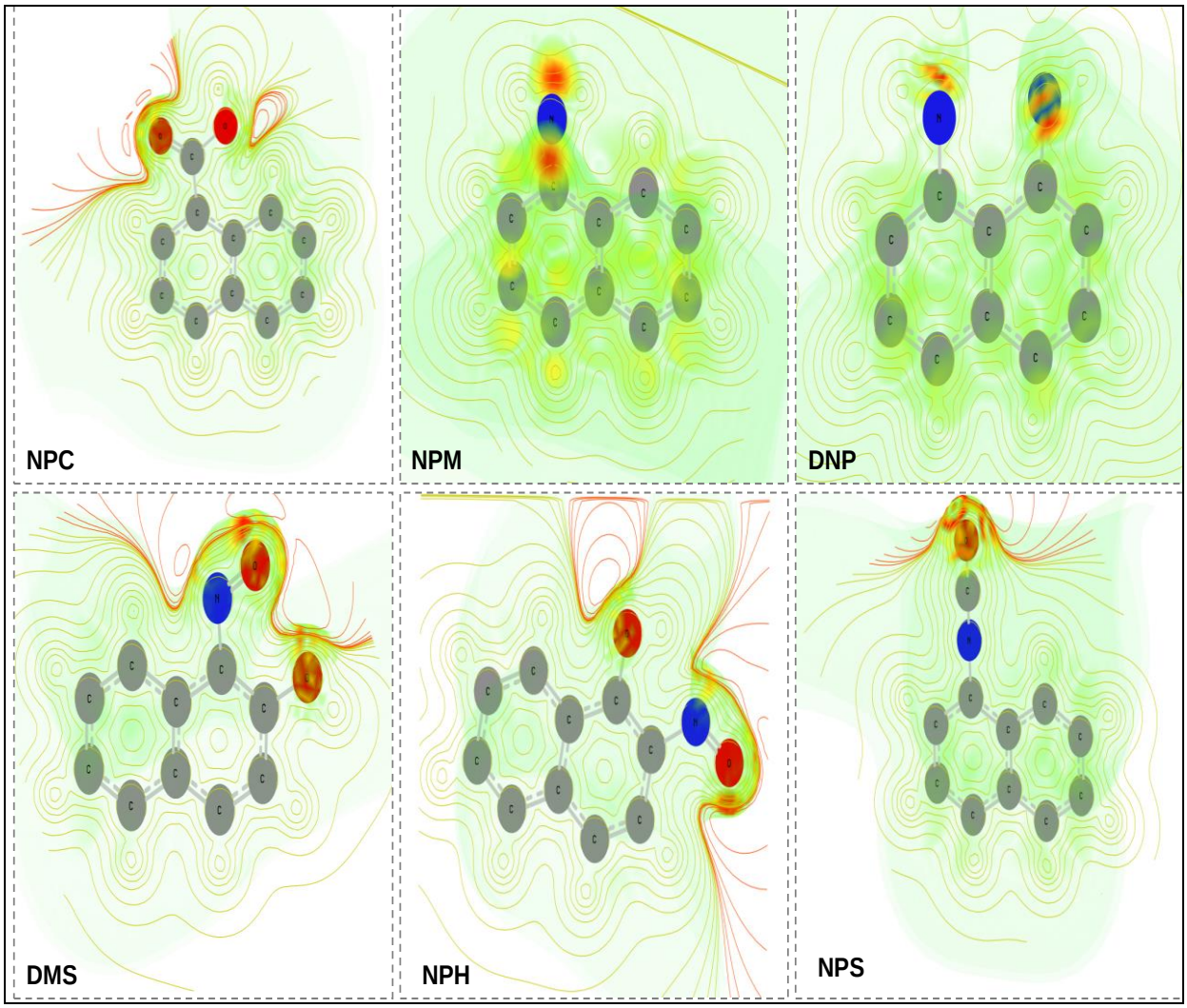


Figure 8. Images of the APT-charge density surfaces as accumulated over donor atoms of the studied chelates: NPC, NPM, DNP, DMS, NPH and NPS

4. Conclusions

.In summary, we have experimentally and theoretically studied six of naphthalene derivatives that differ from each other in terms of number and type of substituents attached to the naphthalene substrate. The six of naphthalene derivatives are : 1-naphthoic acid (NPC), 1-naphthylamine (NPM), 1,8-diamino naphthalene (DNP), 1-nitroso-2-naphthol (DMS), 2-nitroso-1-naphthol (NPH) and 1-naphthylisocynate (NPS). In the study, the mentioned naphthalene based chelates were employed as chelating agents for three of the most toxic and harmful metal ions, these are Hg(II), Cd(II) and Pb(II). How far each chelate was effective in capturing (extracting) the three metal ions, was investigated and evaluated by determining the percent extraction for every individual interaction between the given chelates and each of the indicated ions. Actually, the percent extraction measures how much of the interacted metal ion was removed by a given chelate when both are brought into contact in the contaminated aqueous sample solution .

Other parameters that might interfere with the binding effectiveness of the chelate were also investigated, from which (a) structure of the chelate (b) structure of the formed complex (c) type and number of substituents on the chelate (d) type and number of donor atoms within the chelate (e

Other parameters that might interfere with the binding effectiveness of the chelate were also investigated, from which (a) structure of the chelate (b) structure of the formed complex (c) type and number of substituents on the chelate (d) type and number of donor atoms within the chelate (e) charge density distribution over the chelate surface (f) other chelate's parameters, including geometry, linearity and stability of the chelate.

5.Study significance

In truth, moving forward with the study's stated objectives is mostly necessitated by the need to better understand the binding activity by which the metal ion is caught by the activated binding sites of the implicated chelator. The ambiguities that surround the chelation process are hoped to be clarified by theoretical calculations using reliable and well-known binding models (Halim 2018; Liu et al., 2014). While establishing the chemical interaction between the two the metal ion and the chelator (Bik'el'e et l.,2015; Boukli-Hacene et a., 2016). Gaining these insights would eventually enable researchers to link the binding properties of chelators with their extraction properties. This inquiry will concentrate on the coordination chemistry factors that are crucial in determining the extraction efficiency and permitting some chelators to be more effective toward one metal ion than the other.

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